**Frustrated Itinerant Magnetism**

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Frustrated magnetic systems are those where there are topological restraints such that all magnetic interactions cannot be satisfied simultaneously. This concept was initially applied to local moment systems; relatively recently it has been realized that in itinerant systems where atoms are close to the magnetic instability condition, frustration can be at the origin of exotic magnetic structures and striking effects in the paramagnetic state. The models and experimental data on these systems will be briefly reviewed.

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I. **Local moment systems**

The word "frustration" was introduced in the context of magnetic systems by Toulouse\cite{Toulouse} to express the type of situation where magnetic interactions cannot all be satisfied simultaneously, so that the ground state is necessarily a compromise. Initially this concept was applied to "classical" model systems where the moment at each site is fixed in magnitude but not in direction. Thus for the one dimensional Ising system of figure (1a), if the near neighbour interaction $J_1$ is either ferromagnetic or antiferromagnetic while the next nearest neighbour interaction $J_2$ is antiferromagnetic, the two types of interaction cannot be satisfied simultaneously. In general for near neighbour interactions topological frustration occurs when in a lattice the number of antiferromagnetic interactions in a plaquette is odd. This happens for triangular lattices with antiferromagnetic interactions, or for square lattices if the interactions are chosen appropriately (figures 1b and 1c). In addition to regularly frustrated lattices where there is frustration but no disorder among the set of interactions, there are also random systems (spin glasses) where the set of interactions is chosen at random in such a way that there is topological disorder among the interactions as well as (partial) frustration. Thus in the square lattice if each interaction is chosen with random sign, exactly half the plaquettes are frustrated and these frustrated plaquettes are distributed in a random manner.

There are many physical examples of regularly frustrated and randomly frustrated local moment systems, particularly in intermetallic compounds and in alloys where the existence of long range RKKY-like interactions enhances the probability of frustration. Regular rare earth intermetallic compounds with frustrated interactions can show a wide range of complex magnetic phases: anti-phase structures (DyNi$_2$Si$_2$, TbFeSi$_2$), modulated phases (PrNi$_2$Si$_2$), helimagnetism (Tb, Dy, Ho) or non-collinear structures (DyNi, Er Ni$^2$\cite{Campbell}). Some compounds show numerous quasi-degenerate phases which are either commensurate or incommensurate with a "devil's staircase" phase structure as a function of temperature and field. Recently considerable attention has been paid to Kagomé lattices (SrCr$_{5-x}$Ga$_{4+x}$O$_{19}$ and pyrochlore) which are made up of triangular units assembled around hexagons\cite{Kagome}. They are quasi two dimensional and uniformly frustrated; despite their having strong near neighbour interactions they seem to show no long range order at any temperature.

The theory of frustrated local moment systems has been studied extensively, starting from the antiferromagnetic triangular Ising system\cite{Ising}. The major characteristic of frustration is the possibility of having many degenerate ground states. The frustrated system, with or without topological disorder, can be stabilized in degenerate spin configurations which are not related to each other by a global symmetry (inversion on the case of Ising spins or global rotation for Heisenberg spins). A well studied example for classical spins is the 3d ANNNI (Anisotropic Next Nearest Neighbour...
Ising) model. This model assumes Ising spins on a cubic lattice with ferromagnetic interactions $J_0$ in the planes, and competing near neighbour $J_1$ and second neighbour $J_2$ interactions along the $z$ directions. This model shows a rich field of phases where different stacking sequences are stable. A qualitatively similar phase diagram with a succession of commensurate and incommensurate phases is observed in rare earth compounds such as DyGa$_2$ under applied field.

![Diagram](image)

Figure 1. a. Frustration due to competing interactions in a one dimensional ANNNI model. If the second neighbour interaction is antiferromagnetic, whatever the sign of the nearest neighbour interaction the system will be frustrated. b. Topological frustration for Ising spins in a triangle with antiferromagnetic interactions. There is no way in which all the three interactions can be satisfied. c. Topological frustration for Ising spins in a square with three ferromagnetic interactions and one antiferromagnetic interaction of the same strength. One of the interactions must always be frustrated and there are eight alternative lowest energy states.

At finite temperatures, not too far below the temperature where the magnetic order first sets in, in the presence of long range interactions the magnetic phase will tend to be that with a vector of propagation $Q$ such that the transform of the interactions $J(q)$ is maximized. In these modulated or helimagnetic structures different spins have different time average magnetic moments; a famous example is Cr metal which has a modulated antiferromagnetic order. As the temperature is lowered these structures will in general square up and go over to antiphase structures where all spins have their maximum moment.

II. Model Itinerant systems

Up to now we have considered only classical spins whose moments are fixed in amplitude. In itinerant magnetic systems however the local moment is not fixed but depends to a great extent on the molecular fields exerted on it by its neighbours as well as on parameters such as the external field and the pressure. Thus in the canonical Stoner model of ferromagnetism, a metal with a sufficiently high density of states at the Fermi level becomes ferromagnetic at low temperatures by a bootstrap mechanism where each site acquires a moment aided by the interactions with the moments on the neighbour sites. Weak ferromagnets and their excitations (as in ZrZn$_2$ for instance) are well described by this model.

If interactions are topologically frustrated, one can imagine a situation where on the contrary a ground state can exist where neighbour sites conspire to resolve the frustration by annihilating the moment on certain sites. Thus if the correlation energy at a site $U$ is weaker than the intersite interaction strength $J$, then for a triangle of frustrated spins with antiferromagnetic interactions (figure 2) it will be energetically favourable to suppress the moment on one of the three sites, fig. 2b, rather than maintaining the frustration of fig. 2a. (Most "crimes passionnels" follow this pattern.)

![Diagram](image)

Figure 2. a. A frustrated triangle of Ising spins with antiferromagnetic interactions. b. The same triangle where one of the spins has had its moment suppressed.

A very instructive theoretical model has been developed which expresses this idea starting from a Hubbard Hamiltonian for spins on a two dimensional triangular lattice. It is assumed that the on-site Coulomb repulsion $U$ is of the order of the bandwidth $W$ and that the system is close to the magnetic-nonmagnetic instability. In addition the spin sites are assumed to be very anisotropic so that each spin can take the values up, down or zero. The effective spin 1 Hamiltonian can then be written

$$\Delta \sum_i (S_i^2) + 1/2 \sum_{i \neq j} (J_{ij} S_i S_j)$$

where $A$ and $J_{ij}$ are related to the parameters of the Hubbard model. Now if $A$ is positive the $S_i$ can take the three values: $\pm 1$ with a magnetic moment on the site, or 0 when the site is nonmagnetic which is the ground state in the absence of exchange or an external magnetic field. For the model to exhibit the principal effects, it is
sufficient to restrict the interactions to a near neighbour interaction $J_1$ and a second neighbour interaction $J_2$.

At zero temperature the phase diagram as a function of the ratios $\Delta/J_1$ and $J_2/J_1$ shows four phases; as well as a nonmagnetic phase and two antiferromagnetic phases where all the spins have $\pm 1$ moments there is a phase with both magnetic and nonmagnetic sites. As $\Delta$ is positive, forming a magnetic moment costs energy and for certain parts of the phase diagram it is energetically favourable to have zero moment sites. (It can be checked that the total molecular field on the zero moment sites is zero).

![Figure 3a](image)

Figure 3a. The possible zero field states for the spin 1 two dimensional triangular model. o indicates a nonmagnetic site.

If now a magnetic field is applied, a further rich sequence of phases can appear. Thus for the particular case $A = J_1$ and $J_2 = J_1/2$ (antiferromagnetic ground state in figure 3) the magnetization increases as shown in figure 4 with a phase sequence as a function of applied field which includes two phases with zero moment sites. Both in zero field and in field it can be energetically favourable for certain sites to have zero moment, a “mixed” structure.

![Figure 4](image)

Figure 4. The phase diagram as a function of field for the spin 1 two dimensional triangular model with the particular choice of parameters $\Delta/J_1 = 1$ and $J_2/J_1 = 0.5$. The applied field is in units of $J_1$ and the magnetization is relative to the fully magnetized state. (reference 7)

It can be shown that if we have the same Hamiltonian but with classical spins (all orientations permitted) there will never be zero moment sites in the ground
state; the frustration will be sufficiently reduced by a collaborative canting of the spins, figure 5. It is thus essential to have strong anisotropy for zero moment sites to appear in this model. The effect of anisotropy has been discussed in a quantitative Hubbard model[9], where phase diagrams are given including antiphase and mixed phases as in the discussion above, but also helicoidal and sine wave phases. The form of the phase diagram depends on the relative strengths of the correlation energy $\Delta$, the anisotropy $D$, the couplings and the magnetic field. Mixed structures appear for finite $D$ or field and one can estimate what dose of anisotropy is necessary for a mixed structure to appear. Alternatively even with zero anisotropy if the structure can deform (exchange magnetostriction), a mixed structure can be stabilized by distortion. Finally we can note that magnetic sites always have larger volumes than non-magnetic sites so mixed structures will be associated with a diminution in volume.

![Figure 5. Two possible lowest energy state configurations for a frustrated triangle of XY spins.](image)

**III. REMn$_2$ structures**

The discussion given above may seem over simplified but it turns out that it provides a remarkably cogent explanation of the exotic magnetic structures observed experimentally in the intermetallic compounds REMn$_2$.

There are three main families of RE-Mn intermetallic compounds: REMn$_{12}$, RE$_6$Mn$_{32}$ and REMn$_2$. In all of these the Mn-Mn interactions are antiferromagnetic and the structures are such that two nearest neighbours can be nearest neighbours of each other as in a triangular structure or a tetrahedron, so the conditions for frustration are fulfilled. The REMn$_2$ series is particularly interesting as in addition the Mn moments are close to the conditions for instability of band magnetism. The compounds form in the hexagonal C14 or F.C.C. C15 Laves phases; in both structures Mn atoms are at the summits of regular tetrahedra, which form chains in the hexagonal case and a diamond superstructure in the cubic case. Indirect evidence shows clearly that the the Mn sites in these compounds are strongly anisotropic with in plane moments favoured[9]. The Mn-Mn interactions are an order of magnitude stronger than the RE-Mn or RE-RE interactions so to a first approximation only the former need be considered. There are large magnetovolume anomalies in this series which is the characteristic signature of band moment instability[10].

As a quite general rule in band magnetism, if a site is magnetic it occupies a larger volume than if it is not magnetic; this is the mechanism which gives rise to the invar effect in FeNi alloys, and in the CuMn alloy series at the dilute Mn end where the Mn atoms are strongly magnetic the effective volume occupied by each Mn atom is much larger than near the pure Mn end where the magnetic moments are small. In the REMn$_2$ family it turns out that there is a critical Mn-Mn distance ($d_c = 2.66\text{A}$); when the Mn-Mn separation is lower than $d_c$ as in ScMn$_2$, ErMn$_2$, and HoMn$_2$, the Mn is nonmagnetic and only RE magnetism survives, while for the Mn-Mn distance larger than $d_c$ (PrMn$_2$, NdMn$_2$, GdMn$_2$, and SmMn$_2$) the Mn moments are large (about $2.7\mu_B$) in the ordered state. A fairly large increase in volume takes place at the magnetic ordering transition, indicating that in the paramagnetic state the fluctuating local moments on the Mn sites are lower than in the ordered state. The most striking effects are seen for the two compounds YMn$_2$ and TbMn$_2$, where the Mn-Mn distance is close to the critical value. There are giant increases in volume on ordering (a few percent volume change) with strong hysteretic effects on temperature cycling[10]. Chemical pressure can modify the magnetic ordering considerably in these marginal cases; thus the replacement of a small fraction of Y by Sc which shrinks the lattice eliminates the magnetic order; inversely the introduction of La expands the lattice and stabilizes the magnetism[11]. To summarize, this family of compounds thus unite all the different conditions specific to the model outlined above: frustrated interactions, strong anisotropy, itinerant magnetism with magnetic instability. In remarkable confirmation of the model it is precisely in these compounds that “mixed” magnetic structures with coexisting magnetic and nonmagnetic sites are observed.
In DyMn₂ in zero applied field there is a mixed structure where only 25% of the chemically equivalent Mn sites have magnetic moments, the rest having zero moments[12]. In TbMn₂ the magnetic structure in zero field is complex with all the Mn atoms in a magnetic state, but there is a transition to the same "mixed" structure when a magnetic field of 4.5T is applied at 25K or when a few percent of Mn atoms are replaced by smaller Fe atoms[13]. In ThMn₂ which is also close to the critical condition the Mn atoms order in a triangular antiferromagnetic mixed structure[14]. In other compounds of the same family, even if the structure is not mixed the influence of the frustration is very important; in the ordered structures the frustration is resolved with collinear or complex propagation vectors (PrMn₂, NdMn₂[6]) or with a distorted helicoidal modulation (YMn₂[9]). Similar structures can be induced by hydrostatic or chemical pressure[18] in certain other compounds. As one might expect, in all these systems the effects of hydrostatic pressure are dramatic and small changes in pressure acting upon the lattice parameters give huge changes in ordering temperatures[16].

Frustration continues to play an important role in the paramagnetic state where giant spin fluctuations appear. In particular the compound YMn₂ has been intensively studied[17]. The ground state is a helically modiillated antiferromagnet with a long period of 400Å and two modulation modes[6]. If pressure is applied or the lattice is doped with Sc in the place of Y to provide chemical pressure, the ordering is suppressed[18] and the system becomes heavy fermion like with a large electronic specific heat and electron-electron resistivity term[19]. YMn₂ substituted with 3% Sc is paramagnetic down to zero temperature; the electronic specific heat coefficient is 140 mJ/K² which is a value quite comparable with the heavy fermion systems. The giant antiferromagnetic spin fluctuations in the paramagnetic state lead to strongly enhanced paramagnetic neutron scattering about the antiferromagnetic wavevector for a wide range of temperature. The effective local moment on the Mn sites increases strongly with increasing temperature, tending towards the full Mn magnetic moment at very high temperatures. Thus from integration of neutron scattering intensity, in YMn₂ the effective fluctuating local moment increases from about 1 μB at 90K, the ordering temperature, to about 2 μB at 300K[17]. The transport properties in the paramagnetic state reflect the anomalous magnetic behaviour.

If a fraction of Mn atoms are now replaced by Al atoms the quantum spin liquid state transforms to a spin glass state because of local lifting of total frustration which allows static local moments to form[11]. The system closely follows the qualitative behaviour predicted in a model of a fully frustrated lattice with dilution[11]. The formation of a spin glass is accompanied by other changes in physical parameters.

IV. Other transition metal systems

Although the REMn₂ compounds have been the most intensively studied, there are certainly other systems where frustration produces analogous effects on transition metal sites which are close to the condition for instability. In the Laves phase compound TiFe₂, the ordered state is antiferromagnetic with 1/3 of the Fe sites which are nonmagnetic[20]. In field neutron measurements indicate that these Fe sites are not paramagnetic but have zero moments in the same sense as in the REMn₂ compounds. In the compound MnSi₃ which has a very complex magnetic structure the neutron data indicate that there are Mn sites which have zero moments in the ordered state[21]. For both of these compounds frustration can be invoked.

Pure Mn metal has three different structures α, β and γ; β is nonmagnetic, γ is antiferromagnetic with all sites carrying the same moment of about 2μB and α is a complicated noncollinear antiferromagnet with some sites having moments up to 1.8μB and some close to zero[22]. It is possible that this structure may be the consequence of frustration.

Another element which frequently shows moment instabilities is U. In the compound UNi₄B[23] a mixed structure has been shown to exist.

The only systems we have discussed are those with regular atomic structures. It may be possible to extend the ideas to disordered systems. For instance there are spin glass alloys where the local moments are close to the instability condition; in such alloys the local moments may well be not only disordered in the sense that the moment orientations are quasi-random, but there may be associated variations in the moment affi-
plitudes. CrFe alloys may provide an example of this type of behaviour.

V. Instable rare earth moments: CeSb

We have seen that effects specific to itinerant magnetic systems under the influence of frustration appear most clearly in situations where the local magnetic moments are instable. As well as the 3d magnets, one can also search for such effects in rare earth compounds containing Ce or Yb. The typically "heavy fermion" compounds show unstable local moments and indeed certain compounds have characteristics which closely resemble those of the compounds that we have discussed above. A particularly clear example is the semi metal CeSb. This has one of the most complex magnetic phase diagrams ever discovered\[^{24}\]. It crystallizes in a single NaCl structure with a very small crystal field splitting and a very large cube edge magnetic anisotropy. The properties are very sensitive to hydrostatic pressure and to the applied field. In zero field there is a succession of six modulated commensurate phases with different stackings of ferromagnetic planes with up or down magnetization and of nonmagnetic planes; more mixed phases appear in an applied field\[^{25}\]. As all the planes perpendicular to the modulation direction have an internal ferromagnetic (or zero moment) order, and the moment are "squared up", i.e. the moments in all the ferromagnetic layers are equal, the structures can be very conveniently represented by one dimensional figures. Some of the structures are shown in figure 6. The sensitivity of the Ce moment to the various parameters implies a delicate balance between the f-p hybridisation, the crystal field and the frustrated interactions\[^{26}\]. CeSb is a member of the family of Kondo lattices so the sites at which Ce moments are zero can be considered either as "nonmagnetic" or "Kondo". The excitation spectra seem to suggest that the nonmagnetic layers are not zero moment in the sense of the compounds discussed above, but paramagnetic, meaning that they have rapidly relaxing local moments rather than moments which are suppressed by the band structure effects. The ANNNI model\[^{8}\], which may be thought of as a one dimensional model with frustration because of competing nearest neighbour and second neighbour interactions, can provide an excellent framework for understanding the complexity of the magnetic structures and the succession of modulated phases. As in its original version it is an Ising model (each spin either up or down) it cannot provide an interpretation for the zero moment planes in the mixed structures in the same way as the effective spin 1 model outlined above.

\begin{verbatim}
ferro                     ++++++++ ++++++
ferro mixed 1             ++++o++++++  +++++
ferro mixed 2             +++++o++++++
ferro mixed 3             ++++o+++++++
ferro mixed 4             ++++o++++++o++
ferro mixed 5             ++++o+++++0+++0
ferri 1                   ++++++++ ++++++
ferro 2                   +++-+++ ++++++
antiferro mixed 1        +o------o--o-
antiferro mixed 2        -+++o++++o++++
antiferro mixed 3        -+++o++++o---o-
antiferro mixed 4        +o+++---+++++
antiferro mixed 5        +o+++---+++++
ferro 1                   +---++
ferro 2                   +++-+++o---
ferro 3                   +++--+++---++
ferro 4                   +++-++
\end{verbatim}

Figure 6. The modulated magnetic phases of CeSb. The structure is a succession of ferromagnetic or zero moment (001) planes with the magnetic moments along the modulation c axis and so perpendicular to the planes. Up or down magnetization planes are indicated + or -; zero moment planes are indicated o. (reference 25)

VI. Conclusion

Frustration in itinerant systems has a dramatic effect on the magnetic ordering and can produce zero moment sites in the ordered state when the systems are close to the condition for magnetic instability. In the paramagnetic state effects which mimic heavy fermion behaviour appear and the effective local moments are
highly temperature dependent. There are strong hydrostatic pressure dependences at all temperatures. This novel and striking behaviour has only been interpreted relatively recently and there are certainly many other examples of systems which exhibit itinerant frustration waiting to be discovered. It would be very interesting to pursue the discussion of the relationship between frustration and heavy fermion effects.

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References